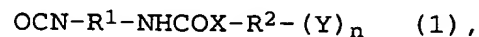


Building blocks containing isocyanate groups and their use for functionalizing or modifying compounds or surfaces

5 The present invention relates to compounds of the formula 1



- where X is a covalent bond to R² or O, S or NR³ and Y is a
- 10 hydrogen atom or a free functional group, a process for preparing them and their use for functionalizing or modifying compounds or surfaces which have at least one group which is reactive toward isocyanate.
- 15 An increasing number of new application areas are being developed both for conventional functionalized monomers or polymeric structures, e.g. for monomeric or polymeric bifunctional, trifunctional or higher-functional alcohols or amines, and also for macromolecular structures having a high degree of branching
- 20 and/or a large number of functional groups on the periphery of the molecule (functionalized macromolecules), for example dendrimers, highly branched and hyperbranched polymers and star polymers. For certain applications, it is necessary to mask particular functional groups of the functionalized monomers or
- 25 polymers or else to vary the functional groups. For example, it can be advantageous to make hydrophilic molecules hydrophobic or hydrophobic molecules hydrophilic. It can also be advantageous, for example, to convert amino groups into hydroxyl groups or carboxyl groups or to transform OH groups into activatable double
- 30 bonds. Furthermore, there is a general need for the functionalization or modification of functional groups on surfaces in order to alter the properties of the surface in an appropriate way.
- 35 WO 97/36857 describes the use of OH-protected trihydroxyalkylaminoalkanes which are converted into a monoisocyanate by means of phosgenation. The resulting isocyanate building block is used to modify isocyanate-reactive groups in dendritic molecules. However, the starting materials used in this
- 40 method of preparing monoisocyanates are synthetically complicated to prepare and the process can only be carried out using small quantities. Furthermore, only groups which are unreactive toward NCO groups can be initially introduced into the macromolecule. The formation of, for example, hydroxyl or carboxylic acid groups
- 45 requires the additional reaction step of ether or ester cleavage.

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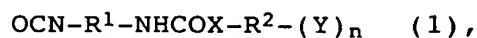
H.W.I. Peerlings and E.W. Meijer, Tetrahedron Lett. 40 (1999) 1021-1024, likewise describe the use of specially prepared alkyl monoisocyanates and aryl monoisocyanates for the surface modification of polyamine dendrimers. Here too, only groups which
5 are unreactive toward isocyanates are introduced into the macromolecule.

Furthermore, R.M. Versteegen, R.P. Sijbesma and E.W. Meijer, Angew. Chem. 1999, 111, 3095-3097, describe the synthesis of
10 $[\eta]$ -polyurethanes in which phosgenation of linear aliphatic α,ω -aminoalcohols is used for the in-situ generation of hydroxyisocyanates which are not stable in the reaction solution and immediately polymerize to form linear polyurethanes.

15 There is therefore a continuing need for building blocks which make it possible to functionalize or modify compounds or surfaces having isocyanate-reactive groups in any desired way.

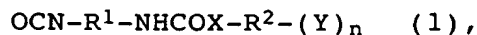
It is an object of the present invention to provide building
20 blocks containing isocyanate groups which can be used for functionalizing or modifying compounds or surfaces having at least one group which is reactive toward isocyanate. A further object of the invention is to provide a process for preparing these building blocks.

25 We have found that this object is achieved by compounds of the formula 1



30 as described in the following text.

The present invention provides compounds of the formula 1,
35 hereinafter referred to as building blocks,

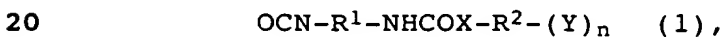


where R^1 and R^2 are each a substituted or unsubstituted, linear or
40 branched, saturated or unsaturated alkylene radical having from 1 to 20 carbon atoms, preferably from 2 to 20 carbon atoms, more preferably from 4 to 20 carbon atoms and particularly preferably from 6 to 20 carbon atoms, a substituted or unsubstituted, saturated or unsaturated cycloalkylene radical having from 3 to
45 20 carbon atoms, a substituted or unsubstituted arylene radical having from 3 to 20 carbon atoms, an arylenealkylene radical having from 4 to 20 carbon atoms, a heterocyclic radical or any

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linear or branched sequence of two or more of the radicals mentioned, if desired linked via ether, thioether, ester, amine or amide structures, X is a covalent bond to R² or O, S or NR³, where R³ is a hydrogen atom or a substituted or unsubstituted, 5 linear or branched, saturated or unsaturated alkyl radical having from 1 to 20 carbon atoms, a substituted or unsubstituted, saturated or unsaturated cycloalkyl radical having from 3 to 20 carbon atoms, a substituted or unsubstituted aryl radical having from 3 to 20 carbon atoms, a heterocyclic radical or any linear 10 or branched sequence of two or more of the radicals mentioned, Y is a free functional group and n is an integer from 1 to 20, preferably from 1 to 5, particularly preferably from 1 to 3. Y can also be a hydrogen atom.

15 The invention further provides a process for functionalizing or modifying compounds or surfaces which have at least one group which is reactive toward isocyanate, by reacting a compound of the formula 1

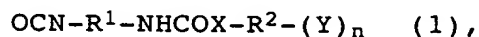


where R¹, R², X, Y and n are as defined above, with at least one isocyanate-reactive group of a compound having at least one isocyanate-reactive group, or with at least one

25 isocyanate-reactive group on a surface which has at least one isocyanate-reactive group.

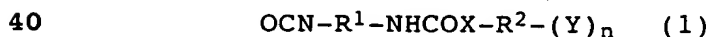
The invention further provides for the use of a compound of the formula 1

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where R¹, R², X, Y and n are as defined above, for functionalizing or modifying compounds or surfaces which have at least one group 35 which is reactive toward isocyanate.

Finally, the invention provides a process for preparing a compound of the formula 1



by reacting a diisocyanate of the formula 2



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with a compound of the formula 3

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where R^1 , R^2 , R^3 , X, Y and n are as defined above and X in formula 3 can also be OCO.

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For the purposes of the present invention, a substituted alkylene radical is an alkylene radical which is substituted at at least one place by a $\text{C}_1\text{-C}_6$ -alkyl radical, a $\text{C}_3\text{-C}_8$ -aryl radical, a halogen atom selected from among fluorine, chlorine, bromine or iodine, or a mixture thereof. The terms substituted cycloalkylene radical, substituted arylene radical, substituted alkyl radical, substituted cycloalkyl radical and substituted aryl radical are defined analogously.

15 For the purposes of the present invention, a free functional group is a reactive position which is not protected by a protective group. Examples of free functional groups which can be used for the purposes of the present invention are hydroxyl, thiol, nitro, substituted or unsubstituted amino, amido, sulfonic acid, sulfenic acid, sulfinic acid, sulfonamide, carbonyl, carboxyl, nitrile, isonitrile, cyanate, isocyanate, thiocyanate, isothiocyanate, silyl, silanyl, substituted or unsubstituted phosphine, phosphoric acid, phosphorous acid, phosphonate, acryl, methacryl, vinyl, allyl and acetylene groups and halogen atoms.

25

In the formulae, Y is preferably a vinyl, allyl, sulfonyl, sulfenyl, sulfinyl, sulfonamide, carbonyl, silyl, silanyl, hydroxy, thiol, carboxyl, sulfonic acid, acryl, methacryl or substituted or unsubstituted amino group.

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Y is particularly preferably a hydroxy, thiol, carboxyl, sulfonic acid, acryl, methacryl or substituted or unsubstituted amino group.

35 For the purposes of the present invention, a substituted amino group is an amino group which is substituted by one or two substituents selected from the group consisting of $\text{C}_1\text{-C}_6$ -alkyl radicals, $\text{C}_3\text{-C}_8$ -aryl radicals, halogen atoms selected from among fluorine, chlorine, bromine and iodine, and mixtures thereof.

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For the purposes of the present invention, a group which is reactive toward isocyanate (also referred to as an isocyanate-reactive group) is a group which bears hydrogen atoms which are reactive toward NCO groups or which can form an addition compound with NCO groups. Examples of such groups are OH, SH, NH, COOH groups, epoxides, acid anhydride or carbodiimide

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groups; among these, preference is given to OH, SH, NH or COOH groups.

- In a preferred embodiment of the building blocks of the present invention, R¹ is a 2,4-tolylene, 2,6-tolylene, 4,4'-diphenylmethylene, 2,4'-diphenylmethylene, 3-alkyl-4,4'-diphenylmethylene, where alkyl is C₁-C₁₀-alkyl, 1,3- and 1,4-phenylene, 1,5-naphthylene, tolidine, biphenylene, tetramethylene, hexamethylene, dodecylene, alkylene lysine ester where alkylene is C₁-C₁₀-alkylene, isophoronylene, 2-methylpentamethylene, 2,2,4- and 2,4,4-trimethyl-1,6-hexamethylene, 1,4-cyclohexylene, 3-methylene-1-methyl-1-cyclohexylene, 2-butyl-2-ethylpentamethylene, 4-methyl-1,3-cyclohexylene, 4,4'- and 2,4'-methylenebis(cyclohexylene), xylylene, tetramethylxylylene radical or a mixture thereof and R² is a linear or branched, saturated or unsaturated alkylene or cycloalkylene radical having from 1 to 20 carbon atoms, a substituted or unsubstituted arylene radical having from 3 to 20 carbon atoms or any linear or branched sequence of two or more of the radicals mentioned which may, if desired, be linked to one another via ether, thioether, amine, amide or ester groups. Mixtures of the specified radicals R² are also possible.
- To prepare the building blocks of the present invention, diisocyanates are reacted with alcohols, thiols, primary or secondary amines or carboxylic acids to form the corresponding addition products. In the case of the reaction with carboxylic acids, this generally proceeds with elimination of CO₂. Particular preference is given to the reaction of diisocyanates with alcohols, thio alcohols and amines.

- The reaction is generally carried out at from 0 to 120°C and the reaction time is usually from 5 minutes to 24 hours. The reaction is preferably carried out under protective gas with or without a solvent, if desired with addition of catalysts customary in polyurethane chemistry. Preference is given to using solvents which are inert toward isocyanate groups. Examples which may be mentioned are benzene, toluene, chlorobenzene, dichlorobenzene, diethyl ether, tetrahydrofuran, dioxane, acetone, 2-butanone, ethyl acetate, butyl acetate, chloroform, methylene chloride, N-methylpyrrolidone, dimethylformamide and dimethylacetamide.

- In a preferred embodiment, diisocyanates whose isocyanate groups have differing reactivity toward the component which is reactive toward isocyanate are used as starting materials. In this case, the building blocks of the present invention are obtained by

In a further embodiment, isocyanates having NCO groups of equal reactivity are used. These are usually reacted in a 2- to 15-fold, preferably 5- to 10-fold, molar excess with the NCO-reactive compound of the formula 3, and the excess isocyanate is subsequently removed.

As isocyanates for preparing the building blocks of the present invention, it is in principle possible to use all organic diisocyanates. Preference is given to using tolylene 2,4-diisocyanate, tolylene 2,6-diisocyanate, diphenylmethane 4,4'-diisocyanate, diphenylmethane 2,4'-diisocyanate, 3-alkyldiphenylmethane 4,4'-diisocyanate, where alkyl is C₁-C₁₀-alkyl, phenylene 1,3- and 1,4-diisocyanate, naphthylene 1,5-diisocyanate, tolidine diisocyanate, biphenyl diisocyanate, tetramethylene diisocyanate, hexamethylene diisocyanate, dodecylene diisocyanate, lysine alkyl ester diisocyanate, where alkyl is C₁-C₁₀-alkyl, isophorone diisocyanate, 2-methylpentamethylene diisocyanate, 2,2,4- or 2,4,4-trimethylhexamethylene 1,6-diisocyanate, 1,4-diisocyanatocyclohexane, 3-isocyanatomethyl-1-methyl-1-isocyanatocyclohexane, 2-butyl-2-ethylpentamethylene diisocyanate, 2-isocyanatopropylcyclohexyl isocyanate, 4-methylcyclohexane 1,3-diisocyanate, dicyclohexylmethane 4,4'- and 2,4'-diisocyanate, 1,3- or 1,4-bis(isocyanatomethyl)cyclohexane, xylylene diisocyanate and tetramethylxylylene diisocyanate (TMXDI).

Particular preference is given to isocyanates having NCO groups
35 of differing reactivity, e.g. aromatic diisocyanates such as
tolylene 2,4-diisocyanate (2,4-TDI), diphenylmethane
2,4'-diisocyanate (2,4'-MDI), 3-alkyldiphenylmethane
4,4'-diisocyanate, where the alkyl radical has from 1 to 10
carbon atoms, or aliphatic diisocyanates such as isophorone
40 diisocyanate (IPDI), 2-butyl-2-ethylpentamethylene diisocyanate,
2-isocyanatopropylcyclohexyl isocyanate,
3-isocyanatomethyl-1-methyl-1-isocyanatocyclohexane, lysine alkyl
ester diisocyanate, where alkyl is C₁-C₁₀-alkyl,
dicyclohexylmethane 2,4'-diisocyanate (2,4'-HMDI) and
45 4-methylcyclohexane 1,3-diisocyanate (H-TDI).

5 isocyanates whose NCO groups are coupled via an electronic system, e.g. phenylene 1,3- and 1,4-diisocyanate, naphthylene 1,5-diisocyanate (NDI), biphenyl diisocyanate, tolidine diisocyanate and tolylene 2,6-diisocyanate (2,6-TDI).

- 10 Particular preference is also given to isocyanates whose NCO groups have equal reactivity but can easily be removed from the reaction mixture by distillation, e.g. tetramethylene diisocyanate, hexamethylene diisocyanate, 1,3- and 1,4-bis(isocyanatomethyl)cyclohexane, tetramethylxylylene 15 diisocyanate, xylylene diisocyanate, diphenylmethane 4,4'-diisocyanate or dicyclohexylmethane 4,4'-diisocyanate.

Mixtures of the isocyanates mentioned can also be used for preparing the building blocks of the present invention.

- 20 The process of the present invention makes it possible to produce and isolate structures which contain both isocyanate groups and groups which are reactive toward isocyanate. Thus, for example, the reaction product of tetramethylxylylene diisocyanate (TMXDI) 25 and diisopropanolamine has one NCO group and two secondary OH groups. It can be isolated as a solid and can be stored for some time (about 24 hours) at room temperature.

Examples of preferred building blocks of the present invention

- 30 are addition products of hexamethylene diisocyanate, isophorone diisocyanate, tetramethylxylylene diisocyanate, tolylene 2,4'-diisocyanate, diphenylmethane 4,4'-diisocyanate, diphenylmethane 2,4'-diisocyanate or p-phenylene diisocyanate and monoalcohols, for example methanol, ethanol, propanol, butanol, 35 hexanol, hexenol, octanol, decanol, dodecanol, octadecanol, octadecenol, allyl alcohol or benzyl alcohol, etherified monoalcohols such as ethylene glycol monomethyl ether, propylene glycol monomethyl ether, polyethylene glycol monomethyl ether or polypropylene glycol monomethyl ether, thio alcohols such as 40 mercaptoethanol, butanethiol or dodecanethiol, monoamines such as methylamine, ethylamine, propylamine, butylamine, dibutylamine, hexylamine, octylamine, decylamine, aniline or benzylamine, polyalkylene oxides functionalized with amino groups, monocarboxylic acids such as acetic acid, propionic acid, butyric 45 acid, hexanoic acid, octanoic acid, decanoic acid or benzoic acid, dialkanolamines such as diethanolamine, dipropanolamine or diisopropanolamine, trialkanolamines such as

- tris(hydroxymethyl)aminomethane or
tris(hydroxyethyl)aminomethane, hydroxycarboxylic acids such as
hydroxyacetic acid, hydroxypropionic acid or hydroxypivalic acid,
mercaptocarboxylic acids such as mercaptoacetic acid or
5 mercaptopropionic acid, aminocarboxylic acids such as glycine,
β-alanine or aminocaproic acid, or aminosulfonic acids such as
taurine. If the acids are used in the form of their salts,
preference is given to sodium, potassium or ammonium salts.
Further possible building blocks are phosphorus-containing
10 compounds such as (2-hydroxyalkyl)triphenylphosphonium salts,
1-(diphenylphosphinoyl)propan-2-ol, aminoethyldiphenylphosphine
or silicon-containing compounds such as trimethylsilylmethanol,
trimethylsilylethanol, dimethylphenylsilylmethanol,
hydroxymethyltriethoxysilane, 3-aminopropyltrimethoxysilane or
15 3-aminopropyltriethoxysilane. Further suitable building blocks
are hydroxy acrylates such as hydroxyethyl acrylate,
hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl
acrylate and hydroxyalkylacrylamides such as
hydroxymethylacrylamide or hydroxymethylmethacrylamide.
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- If a building block of the present invention is used for
functionalizing a compound or a surface which has groups which
are reactive toward isocyanate, it is advantageous but not
absolutely necessary to generate this building block in situ and
25 subsequently to react it with the compound or surface having
groups which are reactive toward isocyanate. The choice of the
isocyanate and the molecular fragment $-(Y)_n$ of the
isocyanate-reactive compound of the formula 3 is made according
to the properties which the compound or surface having
30 isocyanate-reactive groups is to have after functionalization or
modification with the building blocks.

- The functionalization or modification of a compound or a surface
is carried out by bringing the NCO-containing building blocks of
35 the present invention, either in pure form or in a solvent, into
contact with the compound or surface to be functionalized or
modified. The reaction between the NCO groups of the building
blocks of the present invention and the NCO-reactive groups of
the compound or surface to be functionalized or modified
40 preferably takes place at from 0 to 120°C for reaction times of
from 5 minutes to 24 hours, if desired with addition of
catalysts. Here, the building blocks of the present invention can
also be used in a substoichiometric amount, based on the
functional groups of the substrate to be functionalized or
45 modified, in order to carry out, if desired, a partial
modification of the compound or the surface.

5 monomers are OH- or NH-containing substances such as ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, sugar, ethylenediamine, butylenediamine, hexylenediamine or melamine. Examples of polymers are OH-containing polymers such as polyether
0 polyols, polyester polyols, polyacrylate polyols, polyvinyl alcohols, polybutadiene alcohols, NH-containing polymers such as amino-terminated polyetherols, polyalkylenimines, polyalkyleneamines, polyvinylimidazoles, polyamidoamines and polymers containing acid or acid anhydride groups, e.g.
5 polyacrylic acids or polymers containing maleic anhydride groups.

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25 functionalized by, for example, hydroxy, amino, carboxy, thiol or NCO-reactive silane groups.

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The invention is illustrated by the examples below.

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subsequently allowed to react for another 60 minutes at 80°C. The molar ratio of isocyanate to the alcohol was 1:1. Apart from unreacted diisocyanate, the diadduct was formed as by-product, but this could, if desired, be removed by purification operations (chromatography, crystallization). The data for product 4 are shown in Table 1.

Table 1: OH-components as reactants

| Product No. | Isocyanate | Alcohol | NCO content (% by wt.) | Properties |
|-------------|------------|---------------------------|------------------------|---|
| 1 | HDI | Octadecanol | 9.6 | Melting point: 57 - 58 °C |
| 2 | HDI | cis-9-Octadecen-1-ol | 9.6 | Melting point: 28 - 31 °C |
| 3 | HDI | Hydroxyethyl methacrylate | 14.1 | Viscosity at 23°C, 80% in ethyl acetate: 77 mPas |
| 4 | TDI | Hydroxyethyl acrylate | 14.5 | Melting point: 38 - 40°C |

HDI = Hexamethylene 1,6-diisocyanate
TDI = Tolyene 2,4-diisocyanate

1.3. Monothiourethane derived from isophorone diisocyanate (IPDI)

222 g of IPDI (1 mol) were placed in a reaction vessel under a blanket of nitrogen and heated to 50°C. At this temperature, 1 mol of mercaptoacetic acid dissolved in 200 ml of dry chlorobenzene was added dropwise over a period of 30 minutes. The mixture was allowed to react for another 60 minutes at 50°C. The addition product was preferably not purified or isolated, but reacted directly with the molecules or surfaces to be modified or functionalized. The data for the product 5 are shown in Table 2.

1.4. Monoureas derived from diisocyanates and amines or alkanolamines

1 mol of the respective isocyanate was dissolved in 300 ml of THF (dry) and cooled to 10°C. 1 mol of the appropriate amine dissolved in 100 ml of THF was subsequently added over a period of 30 minutes, with the temperature being maintained at 10°C. The mixture was stirred for another 30 minutes at 10°C. The products from TMXDI were found to be surprisingly stable and could be

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stored for some time (about 24 hours) at room temperature without polymerization. The adducts derived from IPDI were preferably not isolated, but reacted directly with the molecules or surfaces to be modified or functionalized. Data for the products 6 to 11 according to the present invention are shown in Table 2.

Table 2: Components containing SH and COOH groups or NH and OH groups as reactants

| Product No. | Isocyanate | Reactive component | NCO content (% by wt.) | Purity (% by area in GPC) |
|-------------|------------|----------------------------------|------------------------|---------------------------|
| 5 | IPDI | Mercaptoacetic acid | 13.4 | 90.0 |
| 6 | IPDI | Dodecylamine | 10.3 | 99.0 |
| 7 | IPDI | Isopropanolamine | 14.1 | 91.0 |
| 8 | IPDI | Diisopropanolamine | 11.8 | 99.0 |
| 9 | TMXDI | Diethanolamine | 12.0 | 89.0 |
| 10 | TMXDI | Diisopropanolamine | 11.1 | 96.0 |
| 11 | TMXDI | Tris(hydroxymethyl)-aminomethane | 11.5 | 91.0 |

IPDI = Isophorone diisocyanate

TMXDI = Tetramethylxylene diisocyanate

2. Modification of macromolecules

2.1. Modification of a polyamine dendrimer having NH₂ functionality 8 as described in WO 93/14147, commercially available as ASTRAMOL® grade from DSM N.V.

The reaction product of HDI and octadecenol (monourethane 2 from Table 1) and dry THF were placed in a reaction vessel and cooled to 10°C. At this temperature, the dendritic polyamine (M = 773 g/mol) dissolved in THF was added over a period of 30 minutes, and the mixture was subsequently stirred at 23°C for another 1 hour. The amount added was calculated so that 1 mol of NH₂ groups of the polyamine per mol of NCO groups was reacted. The product which precipitated was filtered off, washed with THF and dried under reduced pressure at 40°C. Yield: 93% of theory, melting point 119 - 120°C.

While the polyamine dendrimer dissolved, for example, in water or ethanol, the modified product was not soluble in these. However, the modified dendrimer dissolved in, for example, chlorobenzene, n-heptane or isooctane.

2.2. Modification of a polyethylenimine

118 g of the reaction product of HDI and octadecenol (monourethane 2 from Table 1) and 400 ml of dry THF were placed in a reaction vessel. At room temperature (23°C), 10.5 g of polyethylenimine ($M_n = 700$ g/mol) dissolved in 100 ml of distilled water were added over a period of 30 minutes, and this mixture was subsequently stirred at 23°C for another 4 hours. The reaction mixture was admixed with 2 l of acetone, stirred well and allowed to stand for 12 hours. The solid which precipitated was filtered off, washed with acetone and dried under reduced pressure at 40°C.

The yield was 89% of theory and the melting point was 119 - 121°C.

While the polyethylenimine dissolved in water, the modified product was insoluble therein. However, it did dissolve in, for example, chlorobenzene or butyl acetate.

2.3. Functionalization of a high-functionality polyacrylate alcohol

(Lumitol® H 136, BASF AG)
25 g of the adduct of TDI and hydroxyethyl acrylate (monourethane 4 from Table 1) was dissolved in 100 ml of dry chlorobenzene and heated to 40°C. A solution of 68.7 g of Lumitol® H 136 in 100 ml of butyl acetate was added dropwise over a period of 1 hour and the mixture was subsequently stirred at 40°C for 4 hours. After this time, IR spectroscopy no longer detected any NCO bands in the product mixture. Taking off the solvent gave a solid which contained acrylate groups and had a melting range of 31 - 35°C.

3. Modification of surfaces: hydrophobicization of a woven cotton fabric

Two solutions (solution 1 and solution 2) comprising 100 ml of dry tetrahydrofuran and 50 mg of dibutyltin dilaurate were prepared in parallel. 2 g of the adduct of HDI and octadecenol (monourethane 2 from Table 1) were additionally added to solution 1 and dissolved therein. A 5 x 10 cm piece of a woven cotton fabric was subsequently placed in each of the two solutions and the reaction solutions together with the fabric pieces were heated in parallel at 60°C for 2 hours. After cooling, the woven cotton fabrics were taken from the solutions, each washed with 2 x 100 ml of tetrahydrofuran and dried completely by means of a hot air blower. The fabrics were subsequently wetted with water. While the untreated fabric from solution 2 became fully soaked by

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the water, the water all ran off in beads from the monourethane-modified fabric.

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